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(71) Applicant
Shell Internationale Research Maatschappij B.V.

(Incorporated in the Netherlands)

Carel van Bylandtlaan 30, The Hague, Netherlands

(72) Inventor
Elt Drent

(74) Agent and/or Address for Service
D A H Bennett
4 York Road, London, SE1 7NA, United Kingdom

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(54) Preparation of alcohols from olefins

(57) A process for the preparation of an alcohol from the corresponding olefin comprises

a) reacting an olefin with a perfluorinated carboxylic acid in the presence of a very strong sulphonic acid catalyst whose hydrogen-ion activity is greater than that of pure sulphuric acid at a temperature in the range of from -15 to 130°C to afford an ester; and

b) subsequently reacting the ester with water at a temperature in the range of from -15 to 100°C to afford the alcohol and perfluorinated carboxylic acid.

PREPARATION OF ALCOHOLS FROM OLEFINS

This invention relates to the preparation of alcohols from olefins.

For many years, alcohols have been manufactured from olefins by an indirect hydration process in which the olefin is esterified with sulphuric acid, and the resultant sulphate ester is then hydrolyzed to produce the alcohol. However, the process was recognised to have two major disadvantages. Firstly, sulphuric acid is difficult to handle and dispose of. Secondly, the sulphuric acid liberated by the hydrolysis must be concentrated before it can be re-used in the esterification.

In recognition of the disadvantages of the sulphuric acid process, a process was developed for the direct hydration of olefins. In this process, water and the olefin are passed together over a sulphonated cation exchange resin. The sulphonated cation exchange resin is, in effect, sulphuric acid immobilised on a solid support. As the olefin passes across the resin, it reacts firstly with a sulphonate group to afford an ester, and then with water to afford an alcohol and regenerate the sulphonate group. The direct hydration process overcomes the disadvantages of the sulphuric acid indirect hydration process. Unfortunately, it gives a much lower conversion of olefin than the indirect hydration process.

Many attempts have been made to find new processes for the indirect hydration of olefins. Several such attempts focused on a process in which the olefin is first reacted with a carboxylic acid to afford an ester, and the ester is then hydrolyzed to afford the alcohol. Thus, in 1958, United States patent specification number 2,858,331 disclosed a process for preparing alcohols in which an olefin is reacted with a perfluorinated carboxylic acid to afford an ester, and the ester is then hydrolyzed to afford the alcohol. Much more recently, British patent application publication number 2,041,364 and United States patent specifications numbers 4,384,148, 4,461,729 and 4,461,730 disclosed esterification/hydrolysis processes for the preparation of alcohols in which carboxylic acids such as acetic acid are used. In these processes, attention has been focused upon the catalysis of the esterification reaction or on improving the recovery of alcohol following the hydrolysis.

GB-A-2,041,364 discloses an esterification/hydrolysis process for the preparation of secondary butyl alcohol from butenes in which a sulphonated cation exchange resin is used to catalyze the reaction of the butenes with a carboxylic acid. The examples illustrate the use of acetic acid and propionic acid as the carboxylic acid.

US 4,384,148 discloses a process for preparing alcohols from olefins by esterification with a carboxylic acid and hydrolysis, in which alcohol and ether side products are recovered by stripping from the hydrolysis product, separated, and the ether pyrrolyzed to afford more alcohol and olefin. The examples illustrate the use of acetic acid, chloroacetic acid and propionic acid as the carboxylic acid.

US 4,461,729 and US 4,461,730 disclose processes for the preparation of alcohols from olefins by esterification with a carboxylic acid and hydrolysis, in which a zeolite catalyst is used in the esterification. The examples illustrate the use of acetic acid, propionic acid and isobutyric acid as the carboxylic acid.

Surprisingly, it has now been found that alcohols may be prepared with very high conversions from olefins by indirect hydration using a very strong acid as the esterification catalyst and a perfluorinated carboxylic acid as the esterifying carboxylic acid.

Accordingly, the present invention provides a process for the preparation of an alcohol from the corresponding olefin, which comprises

a) reacting an olefin with a perfluorinated carboxylic acid in the presence of a very strong acid catalyst at a temperature in the range of from -15 to 130 °C to afford an ester; and

b) subsequently reacting the ester with water at a temperature in the range of from -15 to 100 °C to afford the alcohol and perfluorinated carboxylic acid.

Preferably the ester is separated from the catalyst after step a). However, it will be appreciated that the catalyst can be recovered after step a) or b), dependent, for example, on the boiling point of the products of steps a) and b) and the ease of separation.

The perfluorinated carboxylic acid is preferably an aliphatic monobasic acid having from 2 to 6 carbon atoms or dibasic acid having 3 to 6 carbon atoms, for example trifluoroacetic acid, pentafluoropropionic acid, heptafluorobutyric acid, perfluoroglutaric acid or tetrafluorosuccinic acid. Most preferably the perfluorinated carboxylic acid is trifluoroacetic acid.

The very strong acids ("superacids") are those acids having a hydrogen ion activity greater than that of pure sulphuric acid as described by R.Stewart in "The Proton-Application to Organic Chemistry", Organic Chemistry, Vol. 46, 1985, Acad. Press Inc. Examples of such superacids are organic perfluorinated sulphonic acids, fluorosulphonic acid, chlorosulphonic acid and acids which can be formed in situ by interaction of a Lewis base with a Broensted acid such as HBF_4 and HPF_6. Preferred acids are perfluorinated sulphonic acids.

The perfluorinated sulphonic acid is preferably an aliphatic acid having from 1 to 8 carbon atoms; for example trifluoromethane sulphonic acid, or a perfluorinated sulphonated cation exchange resin; for example a copolymer of tetrafluoroethylene and a sulphonyl fluoride vinyl ether.

The reaction between the olefin and the perfluorinated carboxylic acid is conveniently conducted in the liquid phase, either in the presence or absence of a solvent.

Suitable solvents for the esterification reaction include organic liquids such as halogenated hydrocarbons, for example methylene chloride, and sulphoxides; for example sulfolane. The perfluorinated carboxylic acid may also act as a solvent.

The amount of perfluorinated carboxylic acid used in the esterification reaction is not critical, but is preferably at least equivalent to the number of moles of olefin groups to be esterified. The number of moles of perfluorinated carboxylic acid per mole of olefin groups is preferably in the range of from 1 to 10, more preferably 1 to 5, even more preferably from 1.1 to 2.5.

The pressure at which the esterification reaction is performed may vary over a wide range. Depending upon the particular olefin, it is conveniently in the range of from 0.5 to 100 bar, preferably from 1 to 50 bar.

If convenient, the esterification reaction may be performed in the presence of inert gases such as carbon monoxide or alkanes. Because of the very high conversion of olefin which is achievable by the process according to the invention, it is attractive to use an olefin-containing hydrocarbon stream from a cracker in the process. In the known processes, which afford lower conversions, this is much less attractive because the unreacted olefin must be recycled, causing a build up of inert hydrocarbons.

The olefin used in the process according to the invention may be a straight chain, branched or cyclic olefin, and may be unsubstituted or substituted by one or more inert substituents, for example alkyl such as methyl, aryl such as phenyl, halogen such as chlorine or fluorine, and alkoxy such as methoxy. Preferably the olefin has from 2 to 20 carbon atoms, more preferably from 2 to 6, most preferably 2, 3 or 4 carbon atoms. Particular examples of olefins are ethene, propene, 1-butene, 2-butene, a mixture of 1- and 2-butenes, cyclopentene and cyclohexene. The olefin may contain 1, 2 or more olefin groups. When the olefin contains 2 or more olefin groups, these groups are preferably non-conjugated.

The preferred temperature for the esterification reaction depends upon the olefin used, for example, when the olefin is ethene, the temperature is preferably in the range of from 70 to 140°C, more preferably 80 to 120°C. When the olefin is propene, or 1- or 2- butene, the temperature is preferably in the range of from 20 to 80°C, more preferably 30 to 70°C. The ester may be separated from the esterification catalyst using a wide variety of techniques, for example distillation, stripping, filtration and liquid-liquid extraction. When the esterification catalyst is a cation exchange resin, it is particularly convenient to filter the olefin and perfluorinated carboxylic acid continuously through it. Alternatively recovery of the catalyst may be effected by similar techniques after step b), although it is preferred to separate the very strong acid after step a) to minimize back reaction to olefin.

The reaction of the ester with water may be performed in the presence or absence of a solvent. Suitable solvents include those which are suitable for use in the esterification reaction, as described above. The reaction may also be performed in the presence or absence of a hydrolysis catalyst. If a catalyst is employed, it is suitably an acid hydrolysis catalyst. If still present, the very strong acid present in step a) can also catalyze the hydrolysis in step b).

Further, since perfluorinated carboxylic acids catalyze the reaction of the ester with water, and since they are produced by this reaction, the reaction of the ester is preferably performed in the absence of an additional hydrolysis catalyst. Thus the reaction of the ester with water is preferably effected by contacting the ester with water, either alone or in the presence of some of the same perfluorinated carboxylic acid as was used in the esterification reaction.

The amount of water used in the hydrolysis of the ester is not critical, but is preferably just sufficient to ensure complete hydrolysis of the ester. Thus, the molar ratio of water to ester is conveniently in the range of from 0.5 to 100:1, preferably 0.75 to 5:1.

The preferred temperature for the reaction of the ester with water depends upon the particular ester. In general, it is from 20 to 140°C, more preferably 30 to 120°C.

The alcohol may be recovered using a wide variety of techniques, for example distillation, stripping and liquid-liquid extraction. Preferably it is recovered by distillation.

When the alcohol has a lower boiling point than the perfluorinated carboxylic acid and the corresponding ester, as is the case with ethanol, isopropanol or secondary butanol with trifluoroacetic acid, for example, the alcohol may very conveniently be recovered by distillation. Generally the alcohol will distil off as an azeotropic mixture with water. The remaining perfluorinated carboxylic acid may then conveniently be recycled to the esterification reaction.

The reaction of the ester with water and recovery of the alcohol may be conducted separately or simultaneously.

Thus the hydrolysis and product recovery may suitably be carried out by a reactive distillation process in which the water addition is continuously controlled to give optimum hydrolysis and product alcohol is continuously removed, the acid generated in the hydrolysis thereby acting as catalyst.

The invention will now be described in more detail in the following Examples.

Example 1

1-Butene (10 ml; 0.1 mol) was pumped into a 250ml Hastelloy C autoclave containing trifluoroacetic acid (20 ml) trifluoromethanesulphonic acid (10 mmol) and sulfolane (40 ml) and heated at 45 °C at autogenous conditions. After 1 hour, analysis of the reaction product showed that almost 100% of the 1-butene had been converted, with a selectivity to 2-butyltrifluoroacetate of 95%.

Example 2

Trifluoroacetic acid (30 ml), trifluoromethane-sulphonic acid (10 mmol) and sulfolane (30 ml) were charged to an autoclave (250 ml). The autoclave was then pressurized with ethene (20 bar) and heated to 120 °C. After 5 hours, analysis of the reaction product showed that 95% of the ethene had been converted, with a selectivity to ethyltrifluoroacetate of greater than 95%.

Example 3

Trifluoroacetic acid (30 ml) and trifluoromethane-sulphonic acid (10 mmol) were charged to an autoclave (250). The autoclave was then pressurized with ethene (20 bar) and carbon monoxide (10 bar) and heated to 100°C. After 5 hours of analysis of the reaction product showed that about 95% of the ethene had been converted, with a selectivity to ethyltrifluoroacetate of greater than 95%.

Example 4

1-Butene (10 ml), trifluoroacetic acid (10 ml) and trifluoromethanesulphonic acid (10 mmol) were warmed in sulfolane (40 ml) at 25 °C. After 5 hours, analysis of the reaction product showed that 90% of the 1-butene had been converted, with a selectivity to 2-butyltrifluoroacetate of greater than 95%.

Example 5

Ethyltrifluoroacetate (10ml) was mixed with water (10 ml) and allowed to stand at ambient temperature overnight. Analysis of the product showed that 30% of the ester had been hydrolyzed to ethanol.

Example 6

1-Butene (10 ml; 0.1 mol), trifluoroacetic acid (20 ml) and "Nafion" NR 501 perfluorinated sulphonated cation exchange resin (10 g: "Nafion" is a trade mark of the DuPont de Nemours Company of Wilmington, Delaware, USA) in sulfolane (40 ml) were heated at 60°C. After 5 hours, analysis of the reaction product showed that about 45% of the 1-butene had been converted, with a selectively to 2-butyltrifluoroacetate of 95%.

Example 7

The crude product of Example 6 was taken, and the cation exchange resin removed by filtration. Water (10 g) was then added to the residual solution, and the mixture allowed to stand at ambient temperature overnight. Analysis of the reaction product showed that about 60% of the ester had been hydrolyzed to secondary butanol.

Example 8

1-Butene (10 mol, 0.1 mol), trifluoroacetic acid (20 ml) and trifluoromethanesulphonic acid (10 mmol) were heated in dichloromethane (30 ml) at 45°C. After 5 hours, analysis of the reaction product showed that 70% of the 1-butene has been converted, with a selectivity to 2-butyltrifluoroacetate of 80%.

Example 9

Trifluoroacetic acid (30 ml), trifluoromethylsulphonic acid (10 mmol) and water (0.5 ml) were added to an autoclave. The autoclave was then pressurized with ethene (20 bar) and carbon monoxide (10 bar), and heated at 100 °C. After 5 hours, analysis of the reaction product showed that 50% of the ethene had been converted, with a selectivity to ethyltrifluoroacetate of greater than 95%.

This Example shows that small quantities of water can be tolerated in the reaction mixture.

Comparative Example 1

The procedure of Example 3 was repeated, but omitting trifluoromethanesulphonic acid. Analysis of the reaction product showed that less than 5% of the ethene had been converted.

Comparative Example 2

1-Butene (10 ml; 0.1 mol), and trifluoroacetic acid (20 ml) were heated in sulfolane (40 ml) at 100 °C. After 5 hours, analysis of the reaction product showed that only 15% of the 1-butene had been converted, with a selectivity to 2-butyltrifluororacetate of 95%.

Comparative Example 3

1-Butene (10 ml; 0.1 mol), trifluoroacetic acid

(20 ml) and concentrated sulphuric acid (10mmol) were heated in sulfolane (40 ml) at 100 °C. After 5 hours, analysis of the reaction product showed that about 40% of the 1-butene had been converted, with a selectivity to 2-butyltrifluoroacetate of 95%.

Comparative Example 4

1-Butene (10 ml; 0.1 mol), acetic acid (20 ml) and trifluoromethanesulphonic acid (10 mmol) were heated in sulfolane (40 ml) at 50°C. After 5 hours, analysis of the reaction product showed that only 60% of the 1-butene had been converted, with a selectivity to 2-butylacetate of 95%.

Comparative Example 5

1-Butene (10 ml; 0.1 mol), trifluoroacetic acid (20 ml) and "Amberlyst" 252 sulphonated cation exchange resin with an ion exchange capacity of about 5.4 meq/g (10g: "Amberlyst" is a trade mark of Rohm and Haas Corp.) were heated in sulfolane (30 ml) at a temperature of 50 °C. After 5 hours, analysis of the reaction product showed that less than 5% of the 1-butene had been converted. Traces of 2-butyltrifluoroacetate were detected.

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CLAIMS

1. A process for the preparation of an alcohol from the corresponding olefin, which comprises

a) reacting an olefin with a perfluorinated carboxylic acid in the presence of a very strong acid catalyst at a temperature in the range of from -15 to 130 ^{o}C to afford an ester; and

b) subsequently reacting the ester with water at a temperature in the range of from -15 to 100 ^{o}C to afford the alcohol and perfluorinated carboxylic acid.

2. A process according to claim 1 wherein the ester is separated from the catalyst after step a).

3. A process as claimed in claim 1 or 2, in which the perfluorinated carboxylic acid is an aliphatic monobasic acid having from 2 to 6 carbon atoms or a dibasic acid having from 3 to 6 carbon atoms.

4. A process as claimed in any one of the preceding claims wherein the very strong acid is a perfluorinated sulphonic acid.

5. A process as claimed in claim 4, in which the perfluorinated sulphonic acid is an aliphatic acid having from 1 to 8 carbon atoms, or a

perfluorinated sulphonated cation exchange resin.

6. A process as claimed in any one of claims 1 to 5, in which the olefin is present in an olefin-containing hydrocarbon stream from a cracker.

7. A process as claimed in any one of claims 1 to 6, in which the olefin is ethene, and is reacted with the carboxylic acid at a temperature in the range of from 70 to 140°C.

8. A process as claimed in any one of claims 1 to 6, in which the olefin is propene, 1-butene or 2-butene, or a mixture of two or three thereof, and is reacted with the carboxylic acid at a temperature in the range of from 20 to 80°C.

9. A process as claimed in any one of claims 1 to 8, in which the very strong acid is perfluorinated sulphonic acid catalyst in the form of a cation exchange resin, and the ester is separated from it by filtration.

10. A process as claimed in any one of claims 1 to 9, in which the reaction of the ester with water is effected by contacting the ester with water either alone or in the presence of some of the same perfluorinated carboxylic acid as was used in the esterification reaction.

11. A process as claimed in any one of claims 1 to 10, in which the alcohol is recovered by distillation in the form of an azeotropic mixture, and the perfluorinated carboxylic acid is recycled to the esterification reaction.

12. A process as claimed in any one of the preceding claims, wherein the reaction of the ester with

water is carried out together with recovery of the alcohol by reactive distillation.

13. A process for the preparation of an alcohol, substantially as described herein and illustrated with reference to Examples 1 to 9.

14. An alcohol when prepared by the process of any one of the preceding claims.

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